

Electrochromic materials for electronic paper

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Abstract Electrochromic materials have the possibility to change their colour reversibly when they are transformed in a differently charged state. By applying an external voltage, charged molecules move towards the electrodes where they accept or donate an electron, and obtain a different colour. When the external voltage is switched off, they return to their initial colour. Recently electrochromism has become very popular because of possible application in electronic paper. Important properties of electrochromic materials are switching time, diffusion and reaction speed. Electrical and optical measurements of electrochromic cells are presented.

Keywords Electrochromism, oxidation and reduction

I. INTRODUCTION

Since time immemorial, mankind has been fascinated by light and how to manipulate it. This curiosity has led to the development of different types of displays. The recent popularity of renewable energy sources and environment issues has however questioned the energy consumption of most of the display technologies, resulting in the development of a whole new generation of paper-like displays, also called electronic paper (fig. 1). The success of these electronic papers has two main reasons. First of all these displays reflect surrounding light, so no backlight is needed and the second reason is that some of the papers are bistable, which means that energy is only required when a pixel is changed. When the voltage is switched off, the image on the display remains.

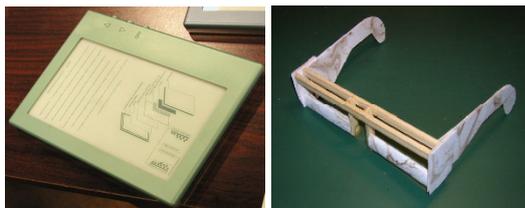


Fig. 1: On the left: The nanochromics technology of Ntera (<http://www.engadget.com/2005/02/15/nteras-nanochromics-display/>)
On the right: Electrochromic sunglasses made at the LCP group

One of the interesting paper-like technologies is the one of electrochromic materials, discovered in 1968 by S.K. Deb and J.A. Chopoorian [1]. The electrochromic molecules, that reversibly change colour when an electron is absorbed or ejected, are manipulated in such a way that they combine with a nanostructured electrode, consisting of TiO_2 (fig. 2) [2-6]. Because electrochromic materials are a special group of the electrochemical materials, reactions between these materials and the electrodes can always be written as $A^{ze^-} + ne^- \rightleftharpoons A^{(z+n)e^-}$, with $z, n \in \mathbb{Z}$. In this paper, measurement techniques are presented to extract physical parameters that characterise electrochromic materials.

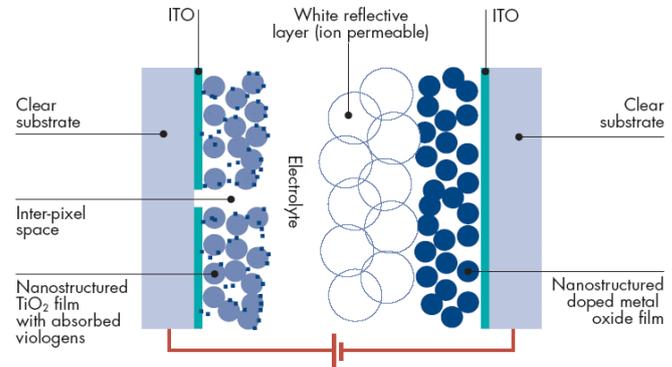


Fig. 2: Cross section of a nanostructured electrode (technology of Ntera [4])

II. EXPERIMENTAL

The investigated solution is a mixture of 2 molecules that have electrochromic properties, solved in propylene carbonate. The concentration of both molecules is about 25 millimolar and one of the two molecules is a type of viologen, also known as bipyridinium, which is a popular electrochromic material [7]. When squeezing this solution between two conducting glass plates, like was done for the sunglasses (fig. 1), full coloring occurs after 4 seconds when a voltage of 1V is applied. The transmission properties of this solution are shown in figure 3.

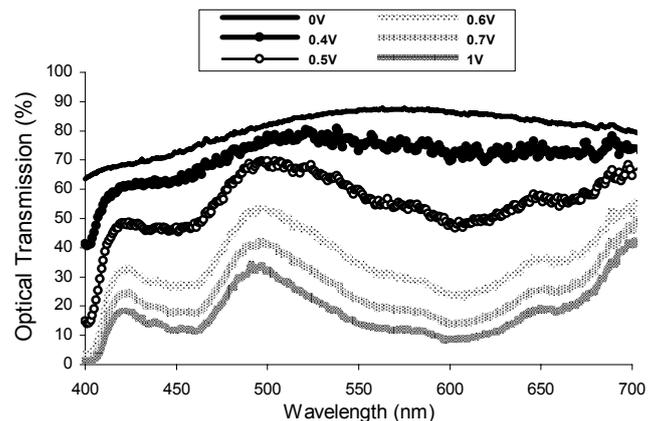


Fig. 3: Transmission spectrum of the investigated solution in function of the applied voltage

III. RESULTS AND DISCUSSION

The solution is investigated in contact with ITO (Indium Tin Oxide) in a potentiostate with Platinum as reference and counter electrodes. The reference electrode is a high impedance electrode and controls the potential on the working electrode, in this case ITO, while the counter electrode's purpose is to close the electrical circuit and to take up the current (fig 4).

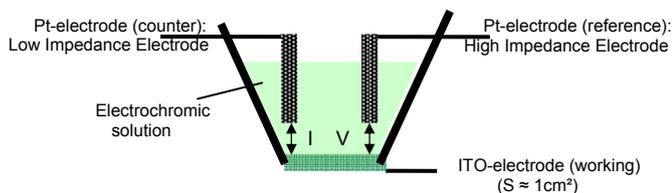


Fig. 4: Schematic representation of a potentiostat

First of all, we try to find the redox potentials. These are the potentials at which the concentrations of A^{ze^-} and $A^{(z+n)e^-}$ near the electrode surface are equal. One way of finding these potentials is through voltammetry, as shown in figure 5. A triangular voltage (slew rate 20mV/s) is applied and the current is measured. At a certain voltage, near the redox potential, the current starts to decrease (arrow 1). At this potential level, the electron transfer rate is fast in comparison to the voltage sweep rate. If the voltage passes this level (arrow 2), the current will decrease because of saturation of the diffusion barrier, so the current becomes proportional to the mass transport rate (arrow 3).

This method is good for low resistive solutions, but because of the higher resistivity of our solution, another method for finding redox potentials is presented.

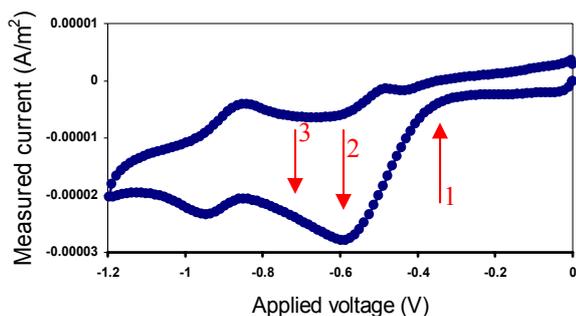


Fig. 5: Voltammogram of the solution showing features of the viologen molecule

Impedance spectroscopy is a useful method for measuring reaction speeds, diffusivities and redox potentials of electrochromic materials. Instead of applying a triangular voltage, a sinusoidal potential is applied (whether superposed on a DC value or not). By using very small AC values, we can assume that the measured current is linear with the applied voltage. The AC value of the current is measured, giving the absolute value of the impedance, and the phase of both the potential and the current are measured. Using a Nyquist plot, the real and imaginary part of the impedance is shown in function of the frequency. This function can be compared with a Randles circuit (fig. 6) which is the electrical analogue of the electrode-solution interface [8-9]. With a curve fitting tool, the parameters of the Randles circuit can be extracted (fig. 7).

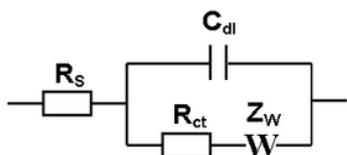


Fig. 6: Randles circuit

(R_s = Resistance of the solution, C_{dl} = Double Layer Capacitance, R_{ct} = Charge transfer resistance and Z_w = Warburg impedance)

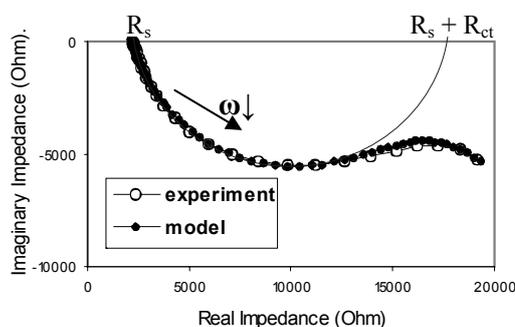


Fig. 7: Nyquist plot of measured and calculated Randles circuit (Randles parameters: $R_s = 2300\Omega$, $C_{dl} = 6 \cdot 10^{-6} F/cm^2$, $R_{ct} = 14680\Omega$, $Z_w = 3700 \Omega/s^{0.5}$, with $V_{DC} = -0.6V$)

Applying this method for several DC values of the potential gives an overview of the potential dependence of all Randles parameters. The minima in the Warburg impedance, which is a parameter that is dependent of the diffusion, correspond with redox potentials of the studied molecules (fig. 7). Knowing the Randles parameters at the redox potentials, allows calculating the diffusion constant and reaction speeds of the molecules. Those are put in a simulation program that calculates the concentration profiles of the different molecules at a certain voltage level and the current flowing through the solution.

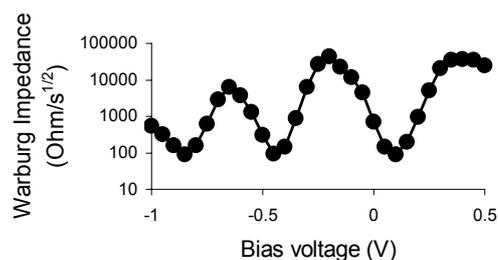


Fig. 8: Voltage dependence of the Warburg impedance. Redox potentials are situated around -0.85, -0.45 and 0.1V.

IV. CONCLUSIONS

Impedance spectroscopy is a powerful tool for extracting diffusion constants and reaction speeds of electrochromic materials. In the near future simulations will be carried out to simulate the detailed behavior of currents and concentrations.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of the European Commission through the sixth framework Integrated Project OLLA—Organic LED's for Lighting Applications. The authors thank Z. Hens and K. Strubbe of the Physical Chemistry department for the use of the potentiostat.

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